

UNCLASSIFIED

AD NUMBER	
AD325602	
CLASSIFICATION CHANGES	
TO:	UNCLASSIFIED
FROM:	CONFIDENTIAL
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAR 1961. Other requests shall be referred to Office of Naval Research, One Liberty Center, 875 North Randolph Street, Arlington, VA 22203-1995.	
AUTHORITY	
31 Mar 1973, Group 4, DoDD 5200.10; ONR ltr dtd 28 Jul 1977	

THIS PAGE IS UNCLASSIFIED

~~CONFIDENTIAL~~

AD 325 602

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



DISCLAIMER NOTICE

THIS DOCUMENT IS THE BEST
QUALITY AVAILABLE.

COPY FURNISHED CONTAINED
A SIGNIFICANT NUMBER OF
PAGES WHICH DO NOT
REPRODUCE LEGIBLY.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

XEROX

~~CONFIDENTIAL~~

Report RMD 076-Q1-61

ARPA Order No. 186-61

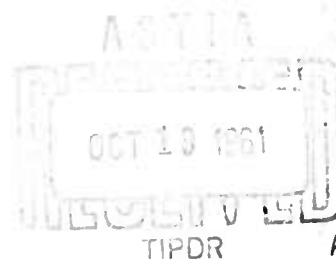
Contract NO. 1878(00)

CATALOGED BY ASTIA 325 602

AS AD No. _____

DIFLUORAMINE CHEMISTRY

Report Period: 20 January 1961 to 31 March 1961



DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DOD DIRECTIVE 5200.10

Thiokol®

CHEMICAL CORPORATION

REACTION MOTORS DIVISION

DENVILLE, NEW JERSEY

~~CONFIDENTIAL~~

Thiokol. CHEMICAL CORPORATION

REACTION MOTORS DIVISION

Effective date of Contract - March 15, 1956
Amount of Contract - \$205,765 CPFF
Expiration Date - December 31, 1961

22142
68

DIFLUORAMINE CHEMISTRY

D. Grafstein
A. Kotloby
A. W. Marcellis
C. Vogel

ARPA- Report RMD 076-Q1-61

Order No. 186-61

Contract NONr 1878(00)

20 January 1961 to 31 March 1961

Submitted by:

M. Cohen

MURRAY S. COHEN
Supervisor
Propellant Synthesis
Section

Project Scientist
Daniel Grafstein
OAKwood 7-7000
Extension 6002

Approved by:

David J. Mann
DAVID J. MANN

Manager
Chemistry Department

for H. Bowman
for Director of Research

~~CONFIDENTIAL~~

Thiokol. CHEMICAL CORPORATION —
REACTION MOTORS DIVISION

RMD 076-Q1

THIS REPORT HAS BEEN DISTRIBUTED IN ACCORDANCE WITH
A COMBINED SPIA-LPIA DISTRIBUTION LIST IN EFFECT AS
OF THE PUBLICATION DATE OF THIS REPORT.

~~CONFIDENTIAL~~

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. DISCUSSION	3
A. Preparation and Characterization of Aliphatic bis-Difluoramines	3
1,2-bis(Difluoramino)cyclohexane	3
Isolation of cis and trans 1,2-bis(Difluoramino)- cyclohexane	3
Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3- hexene and 4,5-bis(Difluoramino)-2,5-dimethyl- 2-hexene	9
1,2-bis(Difluoramino)hexane	13
B. Exploratory Reactions with Aliphatic bis-Difluoramines	13
1,2-bis(Difluoramino)hexane and Triethylamine	16
1,2-bis(Difluoramino)hexane with Sodium Iodide and with Methanol	16
2,5-Dimethyl-2,4-Hexadiene Adducts with Some Basic Reagents	17
III. EXPERIMENTAL	19
Preparation of 1,2-bis(Difluoramino)cyclohexane	19
Preparation of 1,2-bis(Difluoramino)cyclohexane in Flow Reactor	19
Preparation of trans 2,5-bis(Difluoramino)-2,5- dimethyl-3-hexene and 4,5-bis(Difluoramino)- 2,5-dimethyl-2-hexene	19
Separation of Geometrical Isomers	20
IV. FUTURE WORK	21
V. REFERENCES	23

CONFIDENTIAL

Thiokol. CHEMICAL CORPORATION —
REACTION MOTORS DIVISION

LIST OF ILLUSTRATIONS

Figure		Page
1	Vapor Phase Chromatographic Separation of Trans and Cis 1,2-bis(Difluoramino)cyclohexanes	8
2	Infrared Spectrum of Trans 1,2-bis(Difluoramino)- cyclohexane	8
3	Infrared Spectrum of Cis 1,2-bis(Difluoramino)- cyclohexane	8
4	Infrared Spectrum of Trans 2,5-bis(Difluoramino)- 2,5-dimethyl-3-hexene	12
5	Infrared Spectrum of 4,5-bis(Difluoramino)-2,5- dimethyl-2-hexene	12

CONFIDENTIAL

— iv —

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION

REACTION MOTORS DIVISION

LIST OF TABLES

Table		Page
I	Preparation of 1,2-bis(Difluoramino)-cyclohexane	4
II	Mass Spectra of Cis and Trans 1,2-bis(Difluoramino)-Cyclohexane	6-7
III	Reaction of 2,5-Dimethyl-2,4-hexadiene with N_2F_4	10
IV	Mass Spectra of Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene and 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene	14-15

CONFIDENTIAL

— v —

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

ABSTRACT

Substantial quantities of the pure 1:1 tetrafluorohydrazine adducts of 1-hexene, cyclohexene, and 2,5-dimethyl-2,4-hexadiene were prepared. The latter two adducts were resolved into isomers, and structural assignments have been made. As a result, the following pure compounds are now available for the study of C-NF₂ chemistry:

trans 1,2-bis(difluoramino)cyclohexane (I)

cis 1,2-bis(difluoramino)cyclohexane (II)

trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene (III)

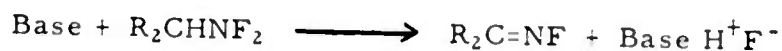
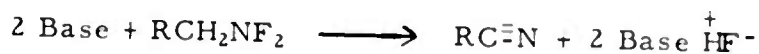
1,2-bis(difluoramino)-n-hexane (IX)

The reactions of these compounds with a variety of reagents are under investigation. Nucleophilic reagents such as alkoxide, t-amine, and iodide primarily cause dehydrofluorination of primary and secondary difluoramines, although other reactions are also observed. Tertiary organic difluoramines apparently are not attacked by these reagents.

Evidence is presented which shows that the addition reaction of tetrafluorohydrazine to olefins is reversed in the mass spectrometer.

I. INTRODUCTION

There are very few well characterized reactions of the aliphatic difluoramines or organoimino fluorides. As a result, our knowledge of the chemical behavior of organic NF compounds is meager. Previous studies (Ref 1) with aliphatic difluoramines containing a hydrogen or a unsaturation disclosed a strong tendency for fluoride elimination or rearrangement. Thus, primary and secondary aliphatic difluoramines undergo dehydrofluorination to yield nitriles and iminofluorides, respectively.



The dehydrofluorination reaction is probably initiated by removal of an α proton by a base with a concurrent or subsequent elimination of fluoride ion. Preliminary evidence suggests that the ease of dehydrofluorination is strongly dependent upon the structure of the aliphatic difluoramine, the strength of the attacking base, and the presence of activating functions on the α carbon atom. Fluorine migration, akin to an allylic rearrangement, has been noted with vinyl difluoramines which are unstable to the formation of β -fluoralkyl iminofluorides (Ref 8). The mechanism for this rearrangement is unknown.



A reaction of C-NF₂ compounds which appears to be characteristic of the NF₂ group is the oxidation of iodide to iodine. The stoichiometry of this redox reaction is not predictable (cf. Ref 2).

Although halogenoid properties have been attributed to the NF₂ group, none of the usual transformations of the organic halides such as organometallic formation, displacement or elimination reactions has been demonstrated with the C-NF₂ group. Also, no substitution or displacement reactions on the fluorine atom of the N-F bond have been described. Thus, a wide area of fruitful research remains to be explored.

CONFIDENTIAL

Thiokol. CHEMICAL CORPORATION

REACTION MOTORS DIVISION

It is the purpose of this program to investigate the chemistry of the aliphatic difluoramines, and to a lesser extent the organo iminofluorides, in order to define the chemical processes which these new functions can undergo.

CONFIDENTIAL

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

II. DISCUSSION

A. Preparation and Characterization of Aliphatic bis-Difluoramines

The initial purpose of this work has been concerned with the preparation of suitable aliphatic bis-difluoramines to supply raw materials for the study of C-NF₂ chemistry. Aliphatic bis-difluoramines are conveniently prepared by the thermal addition of tetrafluorohydrazine to alkenes. 1-Hexene, cyclohexene, and 2,5-dimethyl-2,4-hexadiene were chosen as the starting olefins for the first portion of this work, since their respective N₂F₄ adducts would be expected to be stable, distillable liquids, and each adduct would represent a different kind of C-NF₂ compound. From these adducts a comparison of the behavior of primary, secondary and tertiary NF₂ groups can be made, and this may permit us to distinguish the reactions characteristic of the NF₂ group, independent of the presence of a hydrogen. Both the batch-wise bulb method and the continuous reactor previously described (Ref 1) were used in these preparations.

1,2-bis(Difluoramino)cyclohexane

1,2-bis(Difluoramino)cyclohexane was prepared initially by the bulb reaction of tetrafluorohydrazine with cyclohexene. The early experiments, which show a wide variation in yield, are tabulated in Table I. More recent preparations, both in the bulb reactor and in the continuous reactor, are given in the experimental section. The cyclohexene adduct is a water white, impact insensitive liquid which is easily vacuum distilled, although some decomposition is noted during distillation at higher temperature (> 90°C). A portion of the adduct was triply distilled, and the following properties were measured: bp 46-47°C/6 mm, 118°C/135 mm; $n_D^{27.5}$ 1.4107; d_{25} 1.289g/cc.

Anal. Calcd. for C₆H₁₀F₄N₂: C, 38.71; H, 5.41; N, 15.05; F, 40.83
Found: C, 38.70; H, 5.61; N, 14.86; F, 40.63

Isolation of Cis and Trans 1,2-bis(Difluoramino)cyclohexane

Because of its cyclic structure, cyclohexene adducts could be expected to exist in geometrical forms, i. e. cis (I) and trans (II) isomers:

TABLE I

PREPARATION OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

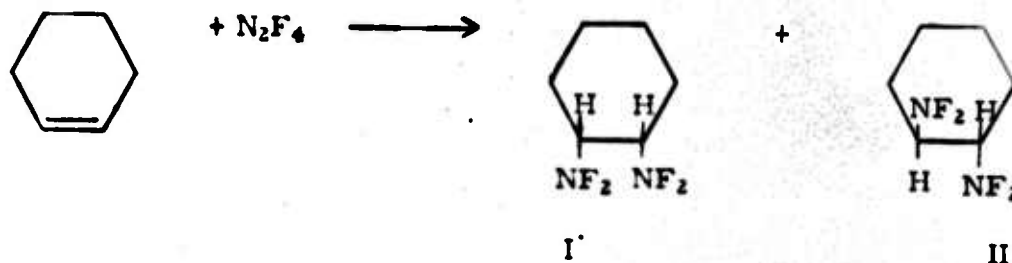
Ex. No. L-374-	Time (hr)	Temp (°C)	Crude Product (grams)	Crude Yield* (%)
44	3	120	2.7	55
47	4	140-145	1.2	24
50	3	120-130	3.28	65
52	3	120-130	1.4	28
56	4	140-145	2.2	44
58	4	140	2.2	44
60	3	125	3.56	71
62	4	120-125	3.1	61
64	2	120-125	3.0	60
66	4	120-125	2.45	50

NOTE: Reactants were 2.2 grams (27 mmoles) cyclohexene and 3.08 grams (31.2 mmoles) 95% N_2F_4 .

* Based on C_6H_{10} charged.

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION
REACTION MOTORS DIVISION



A crude sample of 1,2-bis(disfluoramino)cyclohexane was separated by gas chromatography into two pure components. At $78^\circ C$, column retention times were 49 and 98 minutes (Figure 1). The components were assigned a trans and cis configuration, respectively, based on their infrared spectra and volatilities. These spectra are shown as Figures 2 and 3. As can be seen, the spectra are very similar. The assignment of the cis configuration to the smaller component (98 minutes) is based in part on the presence of the 13.79μ peak in Figure 3 and the absence of this peak in Figure 2.

The components were confirmed as isomers by means of their mass spectra (Table II). The cracking patterns are almost identical. As is usual with these materials, neither component showed a parent peak (m/e 186), but both showed the same highest fragment (m/e 134) corresponding to the removal of one NF_2 group. It may be significant that in both components a strong peak ($r.i. = 100$) appears at m/e 81. This corresponds to the $C_6H_9^+$ moiety and suggests that one of the principal bond breaking reactions is the cleavage of the C-N bond, possibly regenerating the olefin as an intermediate. Some physical constants of the isomers are: trans, d_{25} 1.275 g/cc, n_D^{25} 1.4095; cis, d_{25} 1.293 g/cc, n_D^{25} 1.4125.

Using a larger preparative column, ten liquid cc of the trans-cis mixture were cleanly separated at $135^\circ C$, retention times being 20 and 43 minutes, respectively. Although this method of separation is tedious and limited to relatively small quantities, it appears to be the only practical purification procedure available. Alternative methods for separating the isomers are being investigated. Thus far, liquid phase partition chromatography on a silica column does not appear promising. However, we have some evidence that the mixture can be partially resolved by fractional distillation.

CONFIDENTIAL

Report RMD 076-Q1

TABLE II

MASS SPECTRA OF CIS AND TRANS
1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

m/e	Relative Intensities		m/e	Relative Intensities	
	I Trans	II Cis		I Trans	II Cis
36	0.1	0.1	61	7.8	8.8
37	1.1	1.7	62	3.0	5.3
38	4.0	6.2	63	1.3	1.3
39	48.8	63.5	64	1.0	1.1
40	17.4	22.3	65	11.7	12.9
41	91.4	107.3	66	8.6	10.3
42	31.3	34.7	67	60.3	66.7
43	9.0	10.5	68	16.8	19.4
44	1.8	3.3	69	9.0	10.3
45	2.4	2.9	70	1.8	1.6
46	5.9	7.8	71	1.4	1.3
47	19.2	22.6	72	2.8	3.2
48	8.8	10.2	73	45.3	46.7
49	0.7	0.8	74	10.0	10.3
50	2.1	2.8	75	1.9	1.8
51	7.0	9.4	76	0.9	-
52	6.3	8.2	77	4.6	4.7
53	30.4	35.3	78	1.5	2.0
54	23.3	26.6	79	15.6	15.9
55	26.8	29.3	80	9.7	10.3
56	8.3	7.4	81	100.0	100.0
57	1.9	1.8	82	15.6	16.5
58	1.1	1.4	83	1.7	2.0
59	22.6	24.5	84	1.0	1.0
60	4.1	4.7	85	2.3	2.4

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION

REACTION MOTORS DIVISION

TABLE II (cont)

m/e	Relative Intensities		m/e	Relative Intensities	
	I Trans	II Cis		I Trans	II Cis
86	6.0	6.4	96	6.3	6.5
87	5.2	5.3	97	1.7	1.7
88	2.0	2.0	98	1.6	1.7
89	0.6	0.6	99	5.9	5.8
90	0.4	0.4	100	2.5	2.7
91	0.4	0.4	102	0.2	0.2
92	1.8	1.7	106	0.4	0.4
93	2.1	2.3	110	0.1	0.2
94	6.9	7.0	111	0.3	0.3
95	2.9	3.0	112	0.8	0.7
			114	6.0	6.1
			115	7.3	7.2
			134	3.3	3.4

CONFIDENTIAL

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

1

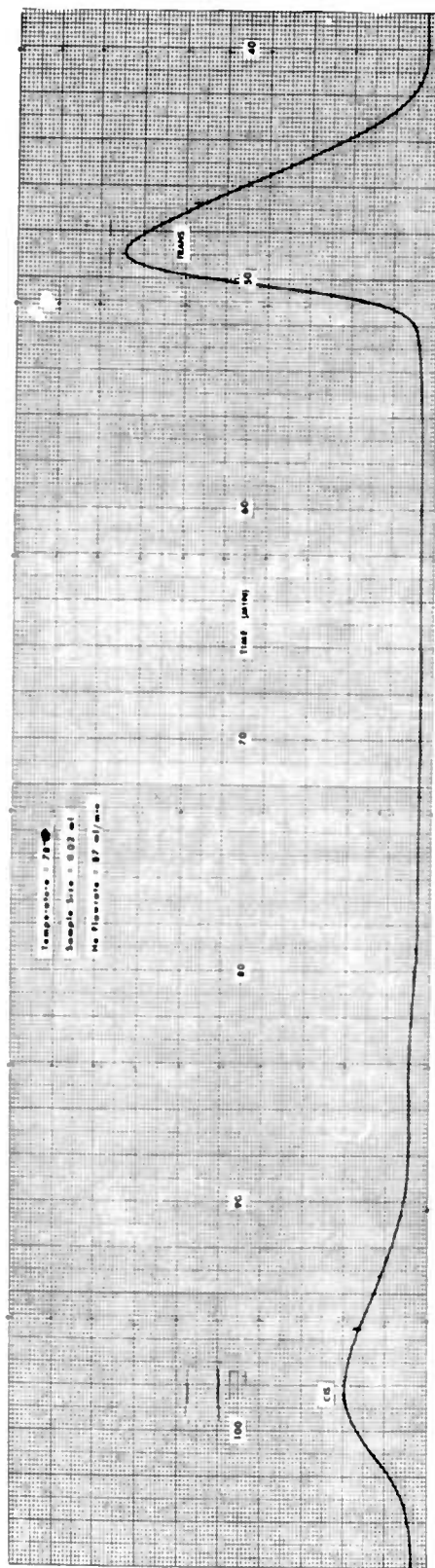


Figure 1. Vapor Phase Chromatographic Separation of Trans and Cis 1,2-bis(Difluoramino)cyclohexanes

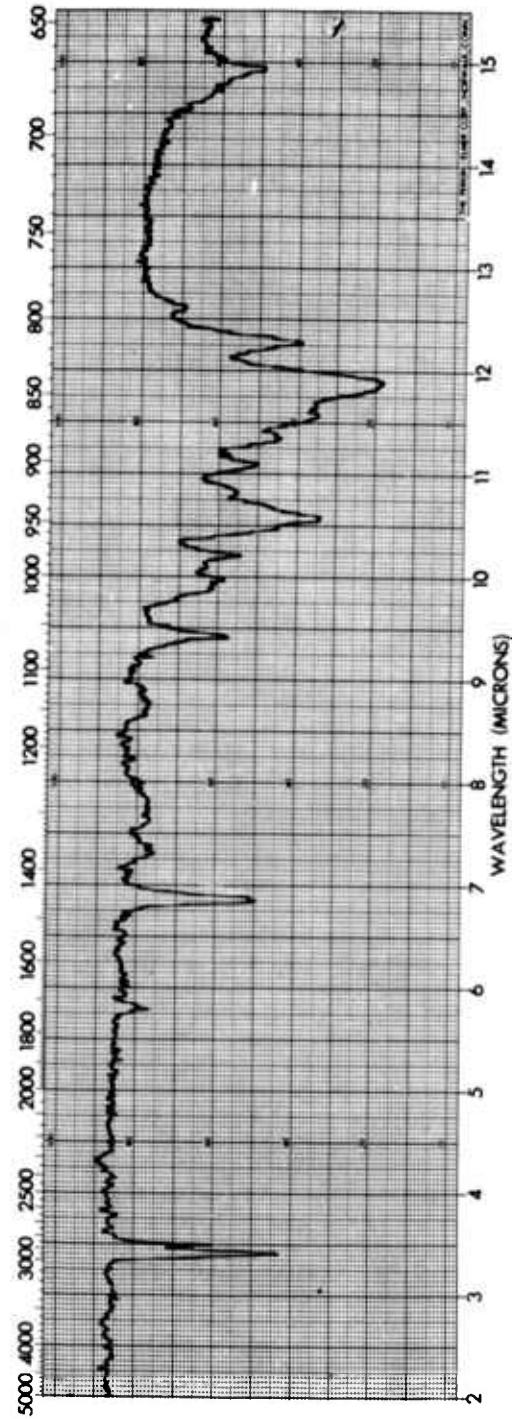


Figure 1. Vapor Phase Chromatographic Separation of Trans and Cis 1,2-bis(Difluoramino)cyclohexanes

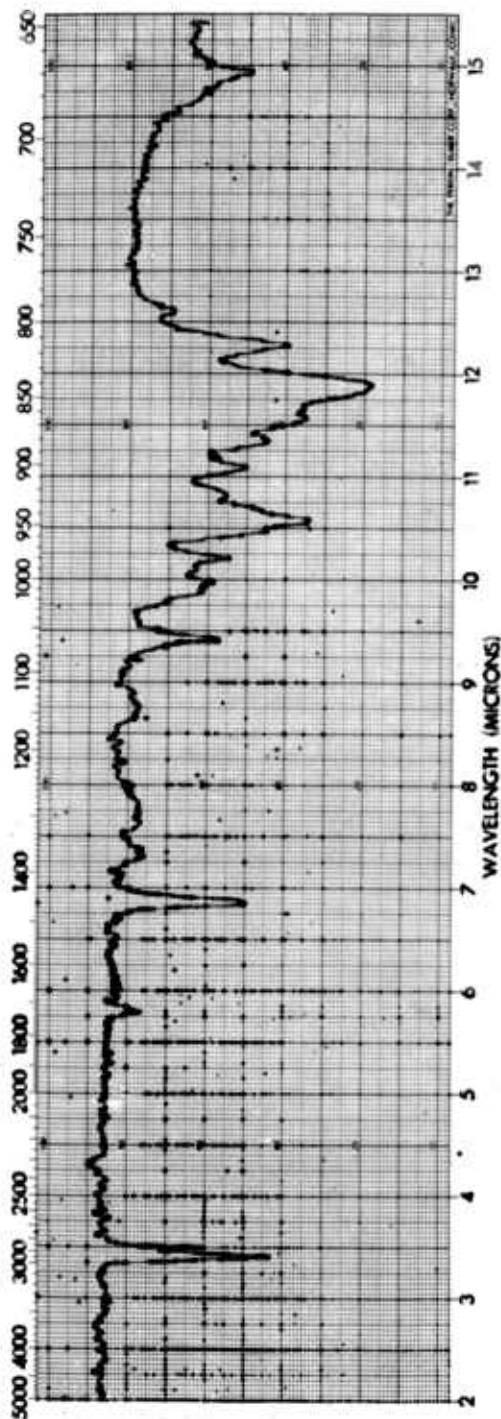


Figure 2. Infrared Spectrum of Trans 1,2-bis(Difluoramino)-cyclohexane

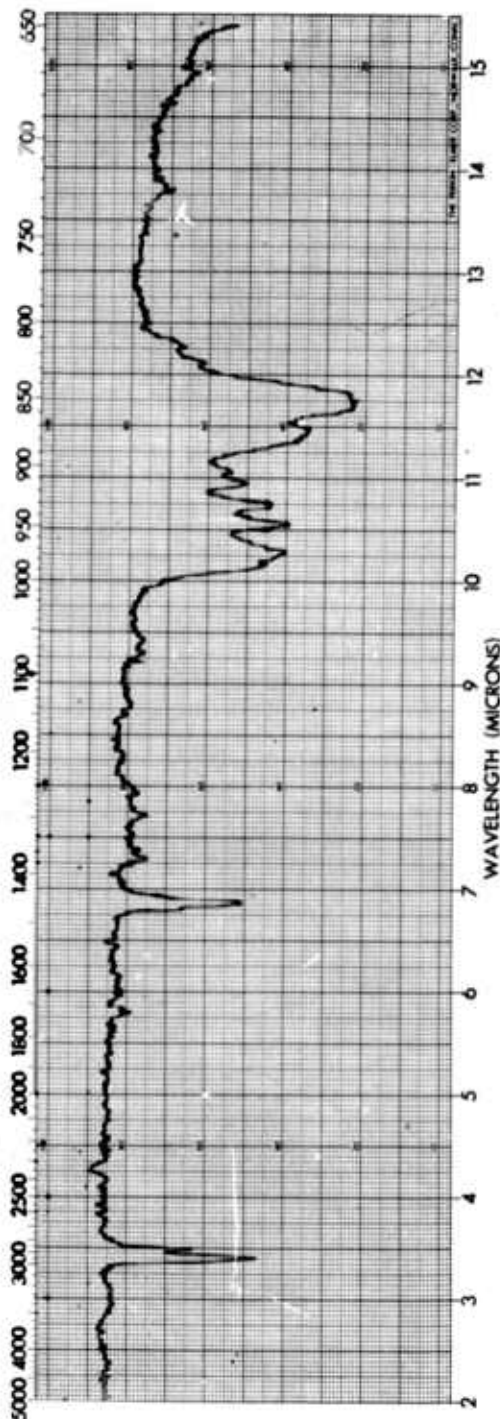
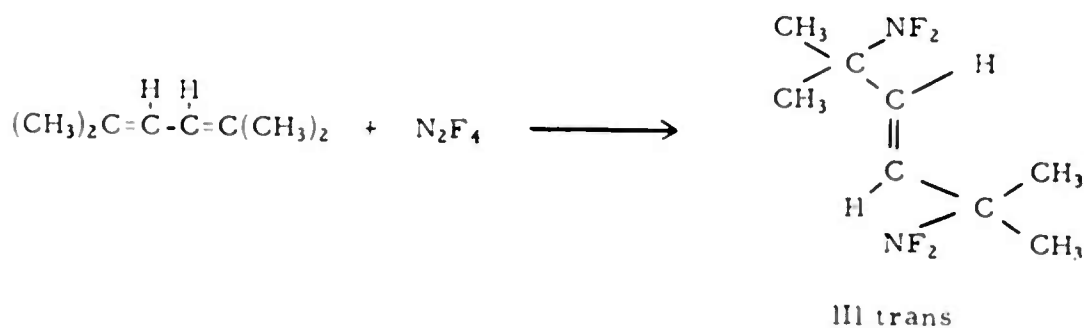


Figure 3. Infrared Spectrum of Cis 1,2-bis(Difluoramino)-cyclohexane

2

Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene and 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene

The reaction of 2,5-dimethyl-2,4-hexadiene with N_2F_4 was investigated in order to prepare a bis-tertiary difluoramine (III) by 1,4 (actually 2,5) addition to the diene system:



Because of steric factors, the trans form of the 2,5 adduct (III) was expected to predominate, and little if any of the cis isomer (IV) was expected. However, another isomer (V), the result of a normal olefin addition, was also a possibility.



Initially, eight bulb reactions were run on this system (Table III) and a red liquid was isolated in yields ranging from 23 to 93%. The combined product was vacuum distilled to give about five grams of colorless liquid as the principal fraction bp 70-73°C/28 mm. The product analyzed well for the desired mono-adduct.

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{F}_4\text{N}_2$: C, 44.85; H, 6.59; N, 13.08; F, 35.48
 Found: C, 44.10; H, 6.80; N, 12.61; F, 34.91

CONFIDENTIAL

Thiokol. CHEMICAL CORPORATION
REACTION MOTORS DIVISION

TABLE III
REACTION OF 2, 5-DIMETHYL-2, 4-HEXADIENE WITH N_2F_4

Ex. No. L-352-	Time (hr)	Temp (°C)	Crude Product (grams)	Crude Yield* (%)
66	4	140-145	2.4	45
68	3.5	100-105	3.67	68
72	8	110	1.25	23
102	4	110-120	3.85	72
104	4	120-135	4.99	93.2
106	4	130-135	4.22	79
108	4	130-135	4.89	90
110	4	130-135	2.45	46

NOTE: Reactants were 85% N_2F_4 (32.3 mmoles) and hexadiene (25 mmoles).

* Based on amount of hexadiene charged.

CONFIDENTIAL

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION

REACTION MOTORS DIVISION

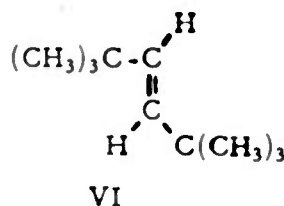
A subsequent set of five runs (see Experimental) gave 16 grams of distilled mono-adduct. This represented a 61% yield. Its physical properties were: bp 92°C/35 mm, n_D^{23} 1.4077.

Anal. Calcd. for $C_8H_{14}F_4N_2$: C, 44.85; H, 6.59; N, 13.08; F, 35.48
Found: C, 44.96; H, 6.60; N, 13.00; F, 35.86

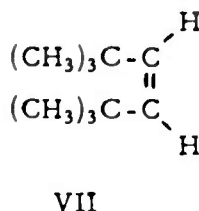
A sample of the second batch of mono-adduct was subjected to gas chromatography and partially resolved into two components, a low melting solid and a liquid. The separation was not clean cut since the peak retention times (50 and 53 minutes at 78°C) were too close and the very small second peak (liquid) overlapped the much larger first peak (solid).

The solid was assigned the trans configuration (III) based initially on its high yield, volatility, and relatively high melting point. Subsequent chemical studies (see below) would appear to strongly support this assignment. The impure liquid (not completely free of III) was at first thought to be the cis isomer (IV), but this assignment was subsequently found to be incompatible with the infrared spectra and apparent reactivity. The infrared spectra of the trans adduct III (Figure 4), and the liquid (Figure 5) are quite similar, except for a double bond peak at 5.98 μ and a peak at 12.28 μ in the latter.

The trans adduct III may be formally compared to trans tertiary butyl ethylene (VI). This molecule was prepared by F. L. Howard, et al. (Ref 3).



The corresponding cis isomer (VII) has been described by G. F. Hennion and T. F. Barrigan (Ref 4).



CONFIDENTIAL

— 11 —

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

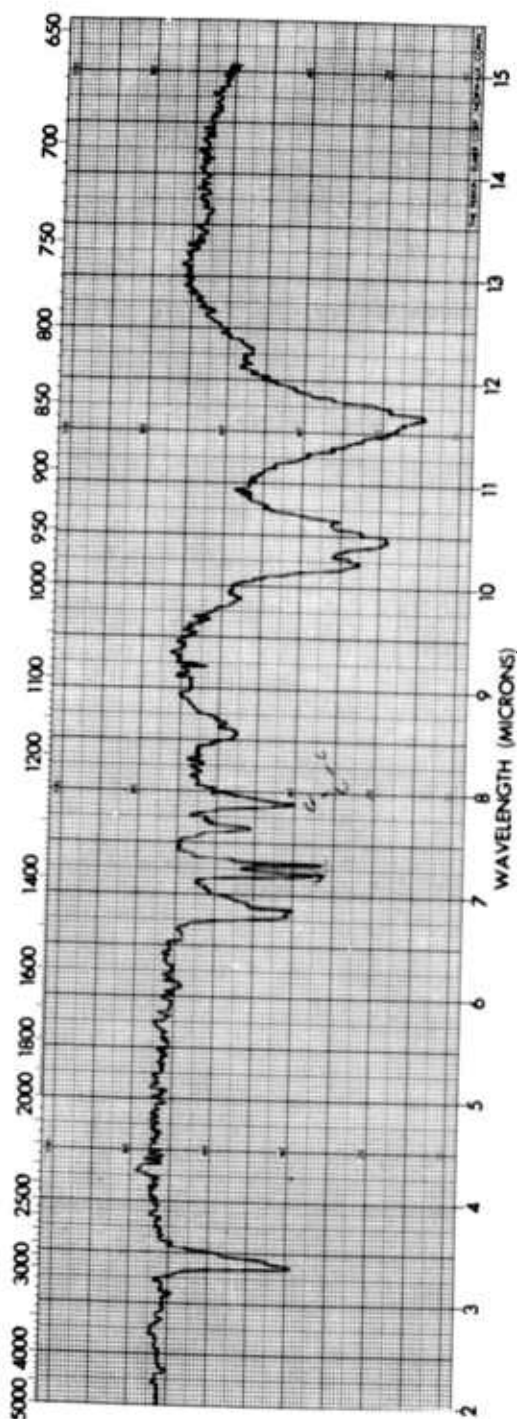


Figure 4. Infrared Spectrum of Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene

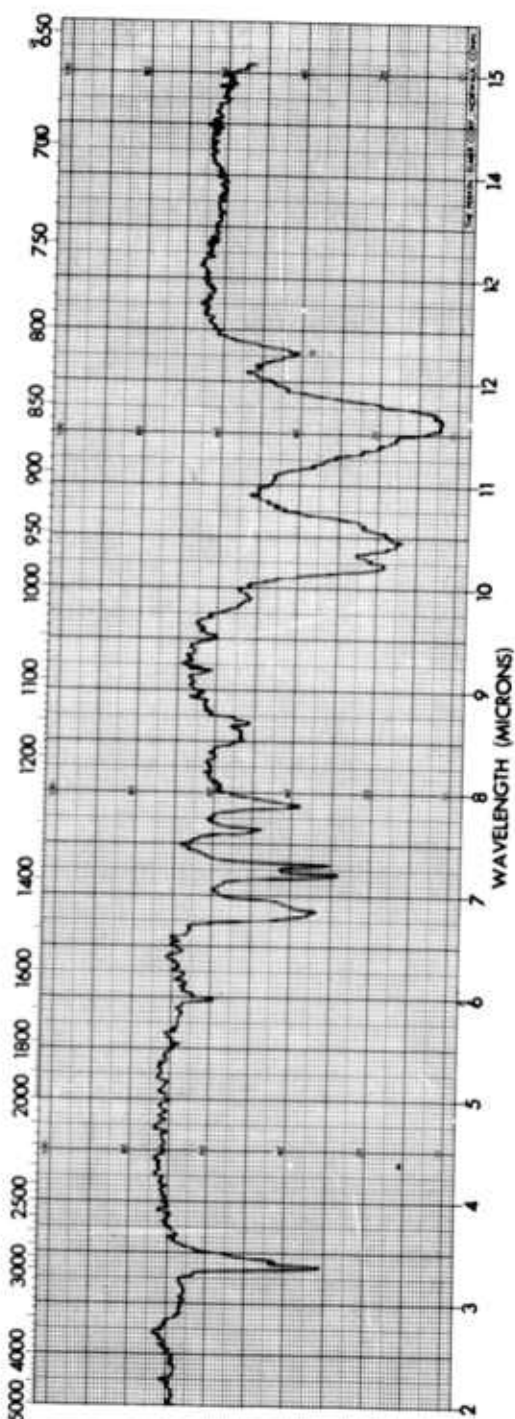
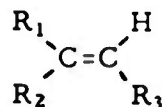


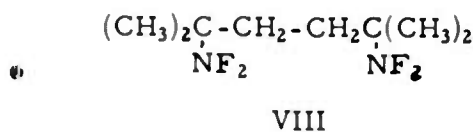
Figure 5. Infrared Spectrum of 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene

The infrared spectra of these isomers were measured by A.R. Bades, et al. (Ref 5). They found that the *cis* isomer (VII) had a characteristic absorption at 13.7μ , while the *trans* absorbed at 10.3μ . It should be noted that our impure liquid product does not possess a 13.7μ absorption but does show a peak at 12.3μ . According to Bellamy (Ref 6), a molecule of the type



has a strong absorption at $840\text{-}790\text{ cm}^{-1}$ ($11.9\text{-}12.8\text{ }\mu$). Consequently, the spectral evidence supports structure V for the liquid isomer.

Mass spectra analysis of III and V confirmed the isomeric relationship (Table IV). Again no parent peak (m/e 214) was observed. However, the peak for the $C_8H_{14}NF_2^+$ fragment (m/e 162) due to the loss of one NF_2 group is noted as the highest mass. Furthermore, a very strong alkadiene peak (m/e 110 r.i. 100) is seen which again supports the previous observation with the cyclohexene adduct that the olefin precursor is probably being regenerated in the mass spectrograph. It will be of considerable interest to see if a non-vicinal, non-conjugated bis-(difluoramino)alkane, such as VIII, would also give rise to a strong hydrocarbon peak.



1,2-bis(Difluoramino)hexane

About 61 grams of crude 1,2-bis(difluoramino)-n-hexane (IX) were prepared in a flow reactor. A portion of this product has been distilled, bp 66-67°C/35 mm, and used in the subsequent chemical studies. Its infrared spectrum was identical to that of the previously prepared pure compound (Ref 1).

B. Exploratory Reactions with the Aliphatic bis-Difluoramines

As pointed out in the introduction, our knowledge of the chemistry of the C-NF₂ group is quite meager. Aside from scattered reports on the variable tendency of primary and secondary aliphatic difluoramines toward dehydrofluorination under basic conditions (for example see Refs 1 and 2), very little

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION

REACTION MOTORS DIVISION

TABLE IV

MASS SPECTRA OF TRANS 2,5-BIS(DIFLUORAMINO)-
2,5-DIMETHYL-3-HEXENE AND
4,5-BIS(DIFLUORAMINO)-2,5-DIMETHYL-2-HEXENE

m/e	Relative Intensities		m/e	Relative Intensities	
	III	V		III	V
26	4.9	2.0	60	2.0	0.9
27	58.6	22.3	61	17.1	3.2
28	41.8	19.7	62	4.1	0.8
29	64.8	17.5	63	1.0	0.6
30	3.9	1.4	65	3.6	4.3
31	0.7	0.3	66	13.8	3.2
32	3.3	2.4	67	12.1	8.7
33	4.8	2.2	68	7.9	4.4
36	0.2	-	69	55.0	7.6
37	0.6	-	70	6.6	1.3
38	2.3	1.3	71	1.6	0.4
39	33.5	21.1	73	2.5	0.8
40	0.3	4.9	74	6.6	1.3
41	113.0	43.8	75	4.9	0.7
42	24.3	10.5	76	1.1	-
43	63.3	17.3	77	2.3	2.8
44	3.9	3.0	78	-	0.8
45	0.8	-	79	4.9	3.2
46	2.9	1.7	80	2.6	1.6
47	30.2	6.4	81	14.6	5.0
48	7.4	1.4	82	5.6	3.3
51	3.3	4.2	83	9.8	1.7
52	2.5	3.3	84	2.0	0.5
53	13.1	13.9	85	0.8	-
54	7.8	6.3	86	0.9	0.4
55	85.5	23.1	87	1.3	0.7
56	20.4	14.4	88	2.8	0.4
57	10.5	2.8	89	0.8	0.2
58	1.6	0.6	91	0.5	0.9
59	5.9	2.9	92	-	0.5

CONFIDENTIAL

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

CONFIDENTIAL

Thiokol CHEMICAL CORPORATION

REACTION MOTORS DIVISION

TABLE IV (cont)

m/e	Relative Intensities		m/e	Relative Intensities	
	III	V		III	V
93	1.0	1.6	109	-	7.9
94	1.6	2.5	110	100.0	100.0
95	19.4	9.2	122	2.3	0.6
96	6.1	6.4	124	3.8	3.2
97	6.1	1.1	126	0.8	0.3
98	-	0.6	128	1.7	1.4
100	-	0.5	139	0.5	-
106	-	0.2	142	0.2	0.3
107	-	0.9	147	0.5	0.3
108	-	2.2	153	0.5	0.1
			159	0.7	-
			162	13.1	12.6

CONFIDENTIAL

Report RMD 076-Q1

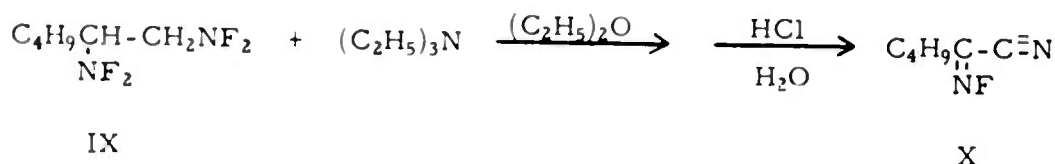
THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

work has been done on the characterization of the reaction products. No one has bothered to determine the behavior of the C-NF₂ group to hydrogenation, reduction, nucleophilic substitution or oxidation. Some work has been done on the oxidation of iodide to iodine (Ref 7) by organodifluoramines but neither the reaction products nor the stoichiometry has been characterized.

The synthesis of aliphatic compounds containing 1°, 2°, and 3° NF₂ groups should provide the tool for studying C-NF₂ chemistry. The tertiary difluoramines are particularly important since the complications due to α hydrogen (i.e. dehydrofluorination) are not present.

1,2-bis(Difluoramino)hexane and Triethylamine

The reaction of 1,2-bis(difluoramino)hexane (IX) with triethylamine was reported (Ref 1) to yield a fluorimino-nitrile, X, identified by its infrared features, a strong C=NF absorption at 5.8 μ, a C≡N band at 4.5 μ and an NF band at 11-12 μ. This reaction was repeated in ethyl ether solvent, and a chromatographically pure sample of iminofluoride-nitrile was isolated after removal of excess triethylamine with hydrochloric acid. It was of interest to note that the strong 5.8 μ band previously observed was no longer present in the pure product and this suggests that the previous sample contained a carbonyl by-product, probably an aldehyde.



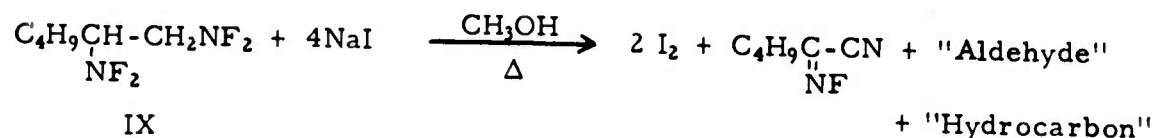
Anal. Calcd. for C₆H₉N₂F: C, 56.24; H, 7.06; N, 21.86; F, 14.83
 Found: C, 55.25; H, 7.31; N, 21.73; F, 15.35

1,2-bis(Difluoramino)hexane with Sodium Iodide and with Methanol

A very complex reaction was observed when IX was treated with sodium iodide in refluxing methanol. About two moles of iodine were liberated per mole of IX. An oil was isolated from the reaction mixture after the iodine was removed with aqueous sodium sulfite. The oil gave an infrared spectrum very similar to X, except that a strong 5.76 μ band was again present. However, the product was resolved into three components by means of gas chromatography. Infrared analysis of the three components indicates that the products

Thiokol. CHEMICAL CORPORATION—

are X, an aldehyde, and a hydrocarbon:



The reaction as written is not logical, since a simple dehydrofluorination of IX would not be expected to liberate iodine. To simplify matters, the behavior of IX toward refluxing methanol was briefly investigated. After 24 hours, a liquid was isolated which appears to be starting material (IX) plus a product containing the 4.43 μ ($C\equiv N$) and 5.76 μ ($C=O$) peaks.

IX was also treated with sodium methoxide in methanol. A vigorous exothermic reaction took place at room temperature. A liquid product, probably a mixture, was isolated. Its spectra showed nitrile and carbonyl bands in addition to some unexpected absorptions at 2.90 μ and 3.07 μ (NH and/or OH), and 6.00 μ and 6.13 μ (double bond region). An attempt will be made to separate this product.

2, 5-Dimethyl-2, 4-Hexadiene Adducts with Some Basic Reagents

Because trans 2, 5-bis(difluoramino)-2, 5-dimethyl-3-hexene (III) contains no α hydrogen, it would be expected to be inert to dehydrofluorination and other reactions requiring removal of an α proton. On the other hand, III might prove to be susceptible to nucleophilic displacement on F, N, or C.

The mixture of III and V was treated with methanol at ambient temperature for 24 hours. After this time, gas chromatography of the solution showed only III in addition to the methanol. In another experiment, 5 mmoles of the mixture were treated with 20 mmoles of sodium methoxide in methanol. After 24 hours, about 4.4 mmoles of the base were consumed. Thereafter, no further change in the base concentration was noted (after five days). Gas chromatography of the solution again revealed solvent and pure III (confirmed by infrared) with a very small second component at some distance from the peak for III. Another sample of the mixture was treated under analytical conditions with refluxing 10% alcoholic potassium hydroxide for one hour, and the resulting solution was tested for its fluoride content after 18 hours. Only about 3% of theoretical 35.5% fluoride content was observed.

CONFIDENTIAL

Report RMD 076-Q1

CONFIDENTIAL

Thiokol. CHEMICAL CORPORATION

REACTION MOTORS DIVISION

The above results indicate that III is inert to strong base and that V is attacked by strong base. This is entirely consistent with the assigned structures. Furthermore, base treatment permits us to remove the small amount of V and isolate pure III from the isomer mixture. It is also significant that III, which cannot undergo dehydrofluorination, does not appear to oxidize iodide to iodine in methanol.

CONFIDENTIAL

Report RMD 076-Q1

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE U.S. WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C. SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

III. EXPERIMENTAL

Preparation of 1,2-bis(Difluoramino)cyclohexane

Cyclohexene (2.7 ml, 0.027 mole) was charged under a constant stream of nitrogen into a 2-liter flask attached to a glass vacuum system. The cyclohexene was cooled to -196°C and degassed. Tetrafluorohydrazine (96% pure, 0.0312 mole, 259 mm Hg) was introduced, and the reactants were heated to 125°C and kept at that temperature for three hours. After this time, the flask was cooled to -196°C , and any noncondensable gases were stripped off under vacuum. The crude product was condensed in a trap cooled with Dry Ice and then collected for distillation. The yield of crude 1,2-bis-(difluoramino)cyclohexane was 3.6 grams (70%). This yield was reproduced three times out of five runs. The other two runs gave only black-brown viscous polymers due to an air leak.

Preparation of 1,2-bis(Difluoramino)cyclohexane in Flow Reactor

A stream of nitrogen diluted N_2F_4 -cyclohexane mixture was passed through a coil reactor (60 cc capacity) kept at 140°C . The flowrates were: N_2 , 16 cc/min; liquid C_6H_{10} , 0.066 cc/min; and N_2F_4 , 11.1 cc/min. This gave a $\text{C}_6\text{H}_{10}/\text{N}_2\text{F}_4$ mole ratio of 1:1. The crude product was collected in a trap cooled at 0°C . A one-day run produced 8-10 grams of crude product. The product contained unknown volatile substances, which sometimes caused ignition. In one instance, the crude product, stored under nitrogen at 0°C , detonated. It proved to be difficult to work with the flow reactor due to the buildup of deposits which tended to plug the coil.

Preparation of Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene and 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene

Under an atmosphere of argon, 2.75 grams (25 mmole) of 2,5-dimethyl-2,4-hexadiene were charged into a two liter bulb. The olefin was then frozen at -196°C , and then the bulb was evacuated. Tetrafluorohydrazine (32 mmole) was introduced, and the reaction flask was heated to $120-150^{\circ}\text{C}$ for four hours. At the end of this time, the mixture was cooled to -196°C and the noncondensable

CONFIDENTIAL

Thiokol. CHEMICAL CORPORATION
REACTION MOTORS DIVISION

gases were pumped off. The residue was distilled into a Dry Ice trap and collected. Five identical runs were made giving 18.6 grams of crude adduct. This was distilled, bp 92°C/35 mm, to give 16.25 grams (61% yield) of the isomer mixture, $n_D^{23} = 1.4077$.

Separation of Geometrical isomers

Gas chromatography of the cyclohexene and dimethylhexadiene adducts was conducted on a Model 154-C Perkin-Elmer Vapor Fractometer. Conditions were:

Column: di-n-decyl phthalate (25%) on fire brick (30-60 mesh), six foot length

Carrier Gas: Helium

Temperature: 78°C

Preparative separation of the cyclohexene adducts was accomplished under the same conditions except that the temperature was 135°C.

CONFIDENTIAL

Report RMD 076-Q1

IV. FUTURE WORK

1. Study the reactions of the organodifluoramines with strong bases, strong nucleophilic reagents, oxidizing and reducing reagents.
2. Hydrogenate trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene to the corresponding hexane.
3. Study the chlorination and nitration of primary and secondary difluoramines.
4. Prepare 1,1-bis(difluoramino)cyclohexane and determine its behavior to iodide and other reagents. Study the chemistry of the gem bis-difluoramino group and determine its possible effects on other functions such as β hydrogen.

~~CONFIDENTIAL~~

Thiokol. CHEMICAL CORPORATION —

REACTION MOTORS DIVISION

V. REFERENCES

1. Thiokol Chemical Corporation, "Superior Liquid Monopropellants," Reaction Motors Division, Report RMD 076-F, July, 1960.
2. Rohm and Haas, P-59-6, II, March 31, 1959.
3. Howard, F. L., Mears, T. W., Forkson, A. and Pomerantz, P., J. Am. Chem. Soc., 68, 2121 (1946).
4. Hennion, G. F., and Barrigan, T. F., J. Am. Chem. Soc., 68, 1202 (1946).
5. Bader, A. R., Buckley, R. P., Leavitt, F. and Swarc, M., J. Am. Chem. Soc., 79, 5621 (1957).
6. Bellamy, L. J., "The Infrared Spectra of Complex Molecules," Methuen Co. Ltd., London, 1958, p 34.
7. Minnesota Mining and Manufacturing Co., Report No. 4, March 31, 1960.
8. Freeman, J. P., et al., Bulletin of the 16th JANAF, III, June 1960, p 105.

UNCLASSIFIED

UNCLASSIFIED